Locality of the Density Matrix in Metals, Semiconductors and Insulators

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Abstract

We present an analytical study of the spatial decay rate γ of the one-particle density matrix $\rho(\vec{r}, \vec{r}') \sim \exp(-\gamma|\vec{r}-\vec{r}'|)$ for systems described by single particle orbitals in periodic potentials in arbitrary dimensions. This decay reflects electronic locality in condensed matter systems and is also crucial for $O(N)$ density functional methods. We find that γ behaves contrary to the conventional wisdom that generically $\gamma \propto \sqrt{\Delta}$ in insulators and $\gamma \propto \sqrt{T}$ in metals, where Δ is the *direct* band gap and T the temperature. Rather, in semiconductors $\gamma \propto \Delta$, and in metals at low temperature $\gamma \propto T$.

Density functional theory (DFT)[1] describes many-body systems via a single-particle formalism and is the basis for modern, large-scale calculations in solid-state systems[2]. The one-particle density matrix $\hat{\rho} \equiv \sum_n |\psi_n\rangle f_n \langle\psi_n|$, which describes the state of a single-particle quantum system, is the key quantity needed for the computation of physical observables: total system energies, atomic forces, and phonons can all be computed directly from $\hat{\rho}$.

Remarkably, despite the de-localized nature of the single particle states $|\psi_n\rangle$, which may extend across an entire solid, the physics of the electronic states in a given region of a material is affected only by the local environment. Reflecting this, the force on an atom depends mostly on the positions of its nearest neighbors. This electronic localization is manifest in the "nearsightedness"[3] of $\hat{\rho}$: $\rho(\vec{r}, \vec{r}') \equiv \langle\vec{r}|\hat{\rho}|\vec{r}'\rangle \sim \exp(-\gamma|\vec{r}-\vec{r}'|)$ where $\gamma > 0$. This exponential decay has been verified numerically[4, 5] and analytically[8, 9, 10, 14].

The locality of ρ not only is important for understanding the nearsightedness of effects arising from electronic structure but also has direct practical impact on DFT calculations. Recently, methods have been proposed [17, 18, 19, 20, 21, 22, 23, 24, 25, 26] that use ρ directly and exploit its locality. Computationally, these methods scale as $O(N)$, where N is the number of atoms in the simulation cell. However, their prefactors depend strongly on γ: some scale as N/γ^6[19, 20, 25] and others as N/γ^3[23]. Knowing how γ depends on the system under study is thus critical for carrying out such calculations. For a review of $O(N)$ methods, see [16].

Generally, solid-state systems have an underlying periodic structure. The introduction of localized defects[8] or surfaces[9] does not change the spatial range of ρ from that of the underlying periodic lattice. Thus, understanding the locality of ρ even for perfectly periodic systems is of direct relevance for realistic material studies. To date, the generic behavior of γ is poorly understood. For insulators in one dimension, Kohn has shown that $\gamma \propto \sqrt{-E_n}$ in the tight-binding limit where E_n is an atomic ionization energy[6]. Motivated by this, it has been assumed[7, 4, 24] and argued[15] that $\gamma \propto \sqrt{\Delta}$ in multiple dimensions and more general conditions, where Δ is the band gap. For metals, it has been assumed[4] and argued[15] that $\gamma \propto \sqrt{T}$, where T is the electronic temperature. However, the results in[15], which to date represent the only effort to determine γ generically, are based on the assumption that the inverse of the overlap matrix of a set of Gaussian orbitals decays in a Gaussian manner. On the contrary, the inverses of such overlap matrices decay only exponentially, and thus the behavior of γ warrants further study.

Here, we show that the behavior of γ is more complex than previously assumed. For insulators, γ is determined by the analytical behavior of the filled bands, which is determined by the strength of the periodic potential which, in turn, is most strongly reflected in the size of the direct band gaps. Indirect

gaps, being more accidentally related to the strength of the potential, have a more haphazard relation to γ, which we do not consider here.

For insulating systems, we find that γ has the following asymptotic behavior as a function of the *direct* gap Δ, lattice constant a, and electron mass m,

$$\gamma \sim \begin{cases} a\Delta m/\hbar^2 & \text{for } a^2\Delta \to 0 \quad \text{(weak-binding)} \\ ??? & \text{for } a^2\Delta \to \infty \quad \text{(tight-binding)} \end{cases}$$

The indeterminacy in the tight-binding limit results from the electronic states becoming atomic orbitals, and thus, γ depends on the details of the underlying atomic potential. Some systems (see below) exhibit $\gamma \propto \sqrt{\Delta}$, but this is *not* universal, as previously assumed.

One can, however, make a definitive statement in the weak-binding limit, which is of direct importance for small-gap systems such as those with weak pseudopotentials or gaps due to Jahn-Teller distortions. For example, semiconductors such as Si and GaAs have gaps that are significantly smaller than their band widths, and we expect them to fall into the weak-binding case. In Si and GaAs, we find $a^2\Delta m/\hbar^2 \sim 4$ and ~ 2.5, respectively. Inspecting Figure 1, we see that for such values the behavior of γ is well in the weakly-bound limit.

For metals with a fixed number of electrons, we find

$$\gamma \sim \begin{cases} k_B T |\vec{\nabla}_k \, \varepsilon|^{-1} & \text{for } T \to 0 \quad \text{(quantum)} \\ \left[\frac{mk_B}{\hbar^2} T \ln\left(\frac{k_B T}{\varepsilon_F}\right)\right]^{\frac{1}{2}} & \text{for } T \to \infty \quad \text{(classical)} \end{cases}$$

in terms of the temperature T, the typical gradient of the band energy $\varepsilon_{\vec{k}}$ on the Fermi surface, and the Fermi energy ε_F.

The low-temperature result is of direct practical interest for calculations in metals. (This result was also found in a contemporaneously submitted publication [14].) We find behavior resembling that proposed in [4, 15], i.e. $\gamma \propto \sqrt{T}$, only at extremely high temperatures.

We now present analytical arguments that substantiate the above results and shed light on the physical mechanisms leading to and differentiating among the different limits. We consider periodic systems with lattice vectors of characteristic length a. We choose units such that $\hbar^2/m = 1$ and $k_B = 1$ in order to avoid cumbersome mathematical expressions; the results presented above are easily recovered by inserting $\hbar^2/m$ and k_B, as appropriate, in each step of the analysis below.

The Bloch wave-functions $\psi_{n\vec{k}}$, Wannier functions W_n, Fermi-Dirac fillings $f_{n\vec{k}}$, and density matrix $\rho(\vec{r}, \vec{r}\,')$ are related via

$$
\begin{aligned}
W_n(\vec{r}, \vec{R}) &= \Omega_B^{-1} \int d\vec{k}\, e^{-i\vec{k}\cdot\vec{R}} \psi_{n\vec{k}}(\vec{r}) \\
F_n(\vec{R}) &= \Omega_B^{-1} \int d\vec{k}\, e^{i\vec{k}\cdot\vec{R}} f_{n\vec{k}} \\
\rho_n(\vec{r}, \vec{r}\,') &= \sum_{\vec{R}} \sum_{\vec{R}'} W_n(\vec{r}, \vec{R})\, F_n(\vec{R}-\vec{R}')\, W_n^*(\vec{r}\,', \vec{R}') \\
\rho(\vec{r}, \vec{r}\,') &= \sum_n \rho_n(\vec{r}, \vec{r}\,').
\end{aligned}
\tag{1}
$$

The integrals are over the first Brillouin zone with volume Ω_B. $\vec{R}$ ranges over the lattice vectors. $\rho_n(\vec{r}, \vec{r}\,')$ is the density matrix of the nth band, and ρ is a simple sum over all ρ_n. Thus, we need only study the behavior of ρ_n for a given n. We analyze the behavior of γ for the two possible cases of practical interest, insulators at low temperature and metals at non-zero temperature.

Insulators (T = 0) — When the chemical potential μ falls in the energy gap, all fillings $f_{\vec{k}}$ are 1 or 0. A filled band with $f_{\vec{k}} = 1$ has $F(\vec{R}) = \delta_{\vec{R},0}$ so that ρ is simply

$$\rho(\vec{r}, \vec{r}\,') = \sum_{\vec{R}} W(\vec{r}, \vec{R}) W^*(\vec{r}\,', \vec{R}).$$

Wannier functions are exponentially localized[5, 6, 7, 8, 9, 11, 12, 13] and satisfy $W(\vec{r}, \vec{R}) = W(\vec{r} - \vec{R}, 0)$. Thus, only a finite set of $\vec{R}$ contribute significantly to the above sum, and the decay rates of ρ and W are the same. Therefore, we need only determine γ for the Wannier functions.

As a concrete example and an initial orientation, we solve exactly for γ for the lowest band of a model one dimensional system for all binding strengths. We choose the periodic potential to be that of an array of attractive delta-functions of strength $V > 0$, $U(x) = -V\sum_n \delta(x - na)$. Following[6], we define $\mu(\varepsilon) \equiv \cos(a\sqrt{2\varepsilon}) - V\sin(a\sqrt{2\varepsilon})/\sqrt{2\varepsilon}$. The band structure is found by solving $\cos(ka) = \mu(\varepsilon_k)$ for real k. Focusing on the lowest band, we denote $\tilde{\varepsilon}$ as the value of ε where $\mu(\varepsilon)$ achieves its first minimum. Kohn [6] has shown that $\gamma = \cosh^{-1}|\mu(\tilde{\varepsilon})|$. We solve the above transcendental system numerically for different values of V and plot $a\gamma$ as a function of $a^2\Delta$ in Figure 1[a]. The behavior at small Δ is clearly linear, showing that $\gamma \sim a\Delta$ for a weak potential. The leading asymptotic behavior is $\gamma \sim \sqrt{\Delta}$ for a strong potential (i.e. large Δ). In this case, the general notion that $\gamma \propto \sqrt{\Delta}$ is clearly incorrect for weak potentials, and it is natural to ask whether this result is peculiar to our simple model or whether it is
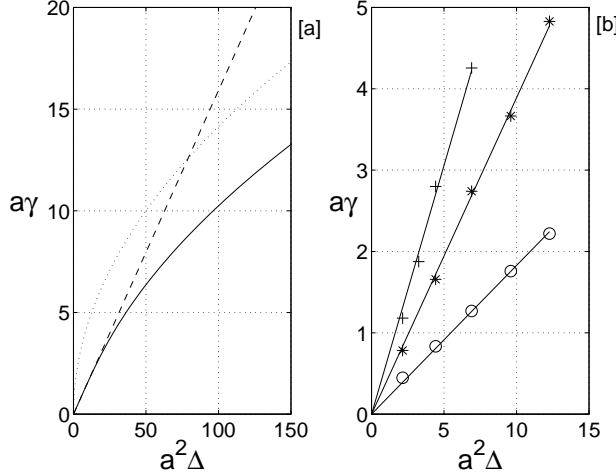
Figure 1: [a] $a\gamma$ versus $a^2\Delta$ for a periodic array of attractive delta potentials (solid curve). The dashed line is $a\gamma = a^2\Delta/(2\pi)$. The dotted curve is $a\gamma = a\sqrt{2\Delta}$, the leading asymptotic behavior of γ for large $a^2\Delta$. [b] $a\gamma$ versus $a^2\Delta$ for a cubic lattice of Gaussian potentials: γ in the [100] (circles), [110] (stars) and [111] (pluses) directions.

more universal. As we now argue, for a weak potential, $\gamma \sim a\Delta$ is quite general, whereas in the case of a strong potential, the behavior of γ is not unique and depends on the details of the atomic system underlying the periodic lattice. The crossover from weak to strong potential behavior should occur when Δ is of order of the band width. In the figure, this occurs for $\Delta \sim 5(\pi/a)^2$. We now analyze each case separately.

Weak-binding insulators in general — We wish to find γ in the limit of a weak periodic potential $U(\vec{r})$. Eqs. (1) show that the Wannier function is the Fourier transform of $\psi_{\vec{k}}$. Thus the range δk in $\vec{k}$-space where $\psi_{\vec{k}}$ has its strongest variations determines the spatial range of W. From basic Fourier analysis, $\gamma \sim \delta k$.

A simple heuristic argument shows that $\gamma \sim a\Delta$. Starting with a free electron description, a weak potential $U(\vec{r})$ causes the opening of a gap Δ at the edges of the Brillouin zone. The extent δk of the region about the zone-edges where $\varepsilon_{\vec{k}}$ deviates most appreciably from its free electron value is given by $\delta k^2/2m^* \sim \Delta$, where m^* is the effective mass at the zone edge. Standard treatments[27] show that for weak potentials $m^* \sim a^2\Delta$. Combining these results, we see that $\delta k \sim a\Delta$, whence $\gamma \sim a\Delta$.

This heuristic argument gives the desired result, but there are hidden assumptions. The argument is based solely on the behavior of the band structure $\varepsilon_{\vec{k}}$,

whereas W is determined by the wavefunctions $\psi_{\vec{k}}$. One must be sure that $\varepsilon_{\vec{k}}$ and $\psi_{\vec{k}}$ vary over the same range δk. Thus, We present a more precise argument in terms of $\psi_{\vec{k}}$ alone.

Letting $\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}u_{\vec{k}}(\vec{r})$, Eqs. (1) show that W is also a Fourier transform of $u_{\vec{k}}$. Away from the edges of the Brillouin zone, $u_{\vec{k}}$ is given perturbatively by

$$u_{\vec{k}}(\vec{r}) = 1 + \sum_{\vec{G}\neq 0} \frac{\langle \vec{G}|\hat{U}|\vec{0}\rangle\, e^{i\vec{G}\cdot\vec{r}}}{\left[k^2 - |\vec{k}+\vec{G}|^2\right]/2} + O(U^2),$$

where $\langle \vec{r}|\vec{G}\rangle = e^{i\vec{G}\cdot\vec{r}}$ and $\vec{G}$ is a reciprocal lattice vector: $u_{\vec{k}}$ is smooth and analytic in $\vec{k}$, and $u_{\vec{k}} \approx 1$. However, close to the zone edges, $|\vec{k}| \approx |\vec{k}+\vec{G}|$ and $u_{\vec{k}}$ deviates appreciably from unity in a region satisfying $[k^2 - |\vec{k} + \vec{G}|^2]/2 \leq V$, where V is the typical size of the matrix elements of U. Since $|\vec{G}| \sim 1/a$, this region has a width $\delta k \sim aV \sim a\Delta$ and hence $\gamma \sim a\Delta$.

As a concrete example, we study a cubic lattice of attractive Gaussian potentials with rms width a/π. We vary the depth of the potential, and for each depth, we compute Δ and ρ by sampling the Brillouin zone on a cubic grid of size 40^3 and expanding $\psi_{\vec{k}}$ in plane waves with $|\vec{G}| \leq 12\frac{\pi}{a}$. Diagonalizing the resulting Hamiltonian gives the ground-state $\psi_{\vec{k}}$ from which we compute the density matrix. Sampling $\rho(0, \vec{r}')$ in the [100], [110] and [111] directions gives exponentially decaying envelopes upon which we perform linear fits on log plots to extract γ. Figure 1[b] shows our results, from which the behavior $\gamma \propto \Delta$ is evident.

Tight-binding insulators in general — The potential U is the periodic sum of an atomic potential V_{at}, $U(\vec{r}) = \sum_{\vec{R}} V_{at}(\vec{r} - \vec{R})$. For sufficiently strong V_{at}, system properties are determined by the atomic potential. The Wannier functions become atomic orbitals localized about the minima of V_{at}. Now, γ depends on the details of V_{at} and no single universal scaling can be found. To demonstrate the complexity and richness of this limit, we discuss briefly different examples of atomic potentials that lead to differing forms for γ. Note that in this atomic limit the lattice constant a is irrelevant in determining γ.

For the Coulomb potential, $V_{at}(\vec{r}) = -Ze^2/r$. In the limit $Ze^2 \rightarrow \infty$, we have hydrogenic states centered on the lattice sites with energies $E_n = -Z^2e^4/2n^2$ and Bohr radii $a_0 = n^2/Ze^2$. The gap Δ is an energy difference between atomic states, and so $\Delta \sim Z^2e^4$. Also, $\gamma \sim a_0^{-1}$, and so we conclude $\gamma \sim \sqrt{\Delta}$. More generally, for any atomic potential with only a single dimensionful parameter (e.g. Ze^2 above), dimensional analysis gives $\gamma \sim \sqrt{\Delta}$.
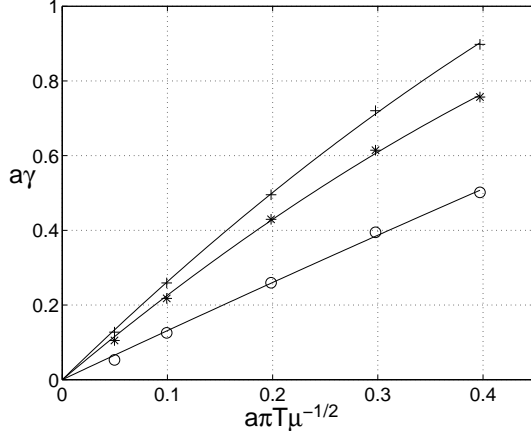
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Figure 2: $a\gamma$ versus $a\pi T\mu^{-\frac{1}{2}}$ for a BCC lattice of tight-binding s-orbitals: γ in the [100] (circles), [110] (stars) and [111] (pluses) directions. μ is measured from the bottom of the band (see text).

However, a similar analysis applied to a Gaussian potential, $V_{at}(\vec{r}) = -Ve^{-r^2/2\sigma^2}$, gives $\gamma \sim \Delta\sigma$, whereas, for a spherical well, $V_{at}(\vec{r}) = -V\theta(\sigma - r)$, we find that γ has *no* dependence on Δ. Thus in the tight-binding limit, it is difficult to make generic statements regarding γ.

Metals (T > 0) — In metals, the fillings $f_{\vec{k}}$ exhibit rapid variations in $\vec{k}$ across the Fermi surface and $F(\vec{R})$ in (1) becomes long-ranged. The Wannier functions, being independent of the fillings, remain exponentially localized, as discussed above. These facts combined with the structure of the sum in (1) imply that γ in this case is determined by $F(\vec{R})$. For an initial orientation, consider a band with a free electron-like form $\varepsilon_k = k^2/2$, whose spherical Fermi surface is contained inside the first Brillouin zone. For such a band, $F(\vec{R})$ is given by (1) with $f_k = 1/\left(1 + \exp\left[(k^2/2 - \mu)/T\right]\right)$. Below, we will use the fact that the density matrix of a true free electron gas is proportional to this F: $\rho(\vec{r}, \vec{r}') \propto F(\vec{r} - \vec{r}')$.

Because the Fermi surface is contained within the first zone, we may extend the $\vec{k}$ integral for F to infinity. Changing to spherical coordinates, integrating by parts and using trigonometric identities yields

$$F(\vec{R}) = \frac{1}{2\Omega_B T}\left(\frac{1}{R}\frac{\partial}{\partial R}\right)^2 \int_{-\infty}^{\infty} \frac{dk\,\cos\left(kR\right)}{\cosh^2\left[\frac{k^2/2 - \mu}{2T}\right]}. \tag{2}$$

When closing the integral in the upper complex k-plane, the relevant poles of the integrand are at $k = \tilde{k}_l \equiv \pm\sqrt{2\mu \pm 2i\pi T(2l + 1)}$ for integers $l \geq 0$. The residues of these poles contain the factor $e^{i\tilde{k}_l R}$ which

gives rise to oscillations due to the real part of $\tilde{k}_l$ and exponential decay due to its imaginary part.

When $T \to 0$, μ equals the Fermi energy $\mu = \varepsilon_F = k_F^2/2$ where $k_F = (3\pi^2 n)^{1/3}$ and n is the electron density. Thus we have $\tilde{k}_l \approx i\pi T(2l + 1)/k_F \pm k_F$. As $R \to \infty$, the $l = 0$ contribution dominates, so that $\gamma = \pi T/k_F$.

As $T \to \infty$, the ideal gas result $\mu \approx T\ln(n\lambda_T^3)$ holds where $\lambda_T = \sqrt{2\pi/T}$ is the thermal de Broglie wavelength. In this limit, $\tilde{k}_l \approx \sqrt{2\mu}$ so that $\gamma = Im\sqrt{2T\ln(n\lambda_T^3)} \sim \sqrt{T\ln(T/\varepsilon_F)}$.

Note that if we approximate the integrand of Eq. (2) by $e^{\mu/T - k^2/2T}$, which corresponds to using Maxwell-Boltzmann fillings, F will have a Gaussian form $F(\vec{R}) \propto e^{-TR^2/2}$. However, one can show that this approximation is only valid for small R. For large R, an exponential tail $e^{-\gamma R}$ remains where γ is as described above.

We now present separate arguments showing that these asymptotic forms for γ are correct for metals in general.

Metals as $T \to 0$ — We first consider first $T = 0$. Bands below the Fermi level then have $f_{\vec{k}} = 1$ and $F(\vec{R}) = \delta_{\vec{R},0}$, and, as for the insulating case, their density matrices decay exponentially. However, for bands that cross the Fermi level, $f_{\vec{k}}$ jumps discontinuously from unity to zero wherever $\varepsilon_{\vec{k}} = \mu$. As is well known, the Fourier transform of a discontinuous function has algebraic falloff, and thus $F(\vec{R})|_{T=0} \propto |\vec{R}|^{-\eta}$ where $\eta > 0$. Such bands therefore dominate the decay of ρ as $T \to 0$.

At finite T, the fillings are $f_{\vec{k}} = (1 + e^y)^{-1}$ where $y = \left(\varepsilon_{\vec{k}} - \mu\right)/T$. As $T \to 0$, the fillings now go from unity to zero in a narrow region about the Fermi surface defined by vectors $\vec{k}_F$ satisfying $|\varepsilon_{\vec{k}} - \mu| \sim T$. To determine the width of this region, we approximate $f_{\vec{k}}$ about the Fermi vector $\vec{k}_F$ via $y \approx \vec{\nabla}\varepsilon \cdot (\vec{k} - \vec{k}_F)/T$. The width of the transition region and γ thus are given by $\gamma \sim \delta k \sim T/|\vec{\nabla}\varepsilon|$. This argument holds for any Fermi surface no matter how complex (metallic or semi-metallic) at sufficiently low T such that δk is smaller than the typical scale of the features of the Fermi surface.

As a further verification for the general case, we study a body-centered cubic lattice of tight-binding s-orbitals with lattice constant $a = 4.32$Å, for which the Fermi surface is non-spherical. We choose the tight-binding matrix element so that the band structure has the free electron effective mass at $\vec{k} = 0$. Choosing μ to be 2/5 of the way from the band minimum to the band maximum, we calculate $F(\vec{R})$ for various values of T. Sampling the Brillouin zone on a 200^3 grid, plotting $F(\vec{R})$ and finding exponentially

decaying envelopes, we perform linear fits on a log plot and extract γ. Figure 2 shows that indeed $\gamma \propto T$ for $T \to 0$.

Metals as $T \to \infty$ — Here the electron kinetic energy is much larger than the periodic potential so that we may approximate $\varepsilon_{\vec{k}} = k^2/2$: the system is a classical ideal gas and is not of interest for solid-state calculations. Our previously derived result for a free electron gas yields $\gamma \sim \sqrt{T \ln(T/\varepsilon_F)}$. Only in this limit do we find a result resembling that of [15].

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